Abrupt "Delta-Like" Doping in Si and SiGe films by UHV-CVD

Field of the Invention

This invention relates to semiconductor films with steep

5   doping profiles and more particularly to forming abrupt "delta-like" doping in thin layers from 5-20nm thick suitable for Si or SiGe CMOS, modulation-doped field-effect transistors (MODFET's) devices, and heterojunction bipolar transistors (HBT's) using in-situ doping in a ultra high vacuum-chemical vapor deposition (UHV-

10   CVD) reactor.

Background of the Invention

In-situ phosphorus doping in epitaxial Si and SiGe films or layers using PH_3 has been known to demonstrate a very slow incorporation rate of P due to the "poisoning effect" of phosphine

15   on the Si(100) surface. An example of such a doping behavior is shown in Figure 1 by curve 11. Curve portion 13-14 of curve 11 shows the slow "transient" trailing edge observed in the SIMS profile and corresponds to the slow incorporation rate of P into the silicon film. In Fig. 1 the ordinate represents P

20   concentration in atoms/cc and the abscissa represents depth in angstroms.

The incorporation of P into a Si layer is increased by the addition of a Ge containing gas (7%) along with phosphine in the reaction zone of a UHV-CVD reactor and has been described in US Patent 5,316,958 which issued May 31, 1994 to B.S. Meyerson and assigned to the assignee herein. The phosphorus dopant was incorporated during UHV-CVD in the proper substitutional sites in the silicon lattice as fully electrically active dopants. The amounts of Ge used were small enough that the primary band gap reduction mechanism is the presence of the n-type dopants at relatively high levels instead of the effect of the Ge. In '958, Fig. 2 shows phosphorus being incorporated into a Si layer during UHV-CVD with and without the addition of 7% Ge containing gas. With 7% Ge containing gas, a decade increase in P concentration would be incorporated in 250 to 500Å into a silicon layer as shown, for example, by the rate of incorporation from 7×10^{18} atoms/cc to 5×10^{19} atoms/cc in Fig. 2 of '958.

Another well known problem associated with in-situ phosphorus or boron doping in silicon CVD is its "memory effect" as shown by curve portion 15-16 in Fig. 1 for the case of phosphorus herein which tends to create an undesirable high level of dopant in the background due to its "autodoping behavior". This "memory effect" is also evident in the SIMS analysis shown in Fig. 1. The "memory effect" corresponds to a very slow fall or decrease in the phosphorus concentration which stems from a residual background autodoping effect. Hence, in-situ doping typically generates a

very undesirable "smearing out" of the dopant profile in silicon films formed by CVD.

Fig. 2 shows curve 11 which is the same as shown Fig. 1 and which illustrates the doping profile of the prior art using PH_3. Curve 20 shows a desired or targeted profile having a width of 100 angstroms. In Fig. 2, the ordinate represents P concentration in atoms/cc and the abscissa represents depth in angstroms. Curve 11 has a dopant profile of at least 5 times wider or thicker than the targeted profile of 100 Angstroms in width or in depth as shown by curve 20.

As device dimensions shrink and especially for future complementary metal oxide semiconductor (CMOS) logic, MODFET's, and HBT's incorporating SiGe layers, very thin layer structures having a width or thickness of 5-20 nm of high doping P concentrations will be needed which are impossible to obtain with present technology at this point using present ultra high vacuum-chemical vapor deposition (UHV-CVD) or standard silicon CVD processing.

Summary of the Invention

In accordance with the present invention, a structure is provided having an increasing or decreasing abrupt doping profile comprising a substrate such as Si or SiGe having an upper surface, a first epitaxial layer of substantially Ge formed over the upper

surface, the first layer having a thickness in the range from .5 to 2 nm and doped e.g. with phosphorus or arsenic to a level of about 5×10^{19} atoms/cc, and a second epitaxial layer of a semiconductor material having any desired concentration of dopants. The second

5   layer may be Si or $Si_{1-x}Ge_x$. The concentration profile from the edge or upper surface of the first layer to 40Å into the second layer may change by greater than 1×10^{19} dopant atoms/cc.

The invention further provides a method comprising the steps of selecting a substrate having an upper surface, growing a first

10   epitaxial layer of substantially Ge thereover less than its critical thickness and doped with phosphorus to a level of about 5×10^{19} atoms/cc, growing a second epitaxial layer selected from the group consisting of Si and SiGe, the second epitaxial layer having any desired doping profile. The presence of the epitaxial Ge layer

15   accelerates the incorporation rate of the P or As doping into the Ge layer, thereby eliminating the slow transient behavior. The initial, in-situ doping level is determined by the dopant flow in SCCM of the PH_3/He mixture. The final overall doping profile may be controlled as a function of 1/GR where GR is the growth rate of

20   the first and second layer. The dopant may be supplied or carried by phosphine (PH_3) or Tertiary Butyl Phosphine (TBP) gas in the case of P and AsH_3 or Tertiary Butyl Arsine (TBA) in the case of As in a UHV-CVD reactor.

To eliminate background "autodoping effect", the structure

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with phosphorus doping as shown in Fig. 3 is transferred to a load chamber or load lock, while the growth chamber is purged of the background phosphorus. This growth/interrupt/growth process involves hydrogen flushing of the UHV-CVD reactor during interrupt.

5   Then, a coating of Si or SiGe is grown on the sidewalls and/or heated surfaces of the UHV-CVD reactor at high temperature to isolate, eliminate or cover the residual phosphorus atoms prior to reintroducing the structure for further deposition. Alternatively, a second growth chamber i.e. UHV-CVD reactor coupled to the load

10   chamber may be used where further undoped layers may be deposited with very low levels of phosphorus.

A second epitaxial layer 40 and/or a third epitaxial layer 44 of Si or SiGe shown in Fig. 3 may now be grown with a background doping profile that drops or decreases to less than 5×10^{16}

15   atoms/cc after a 300Å film is grown over layer 36 of structure 30 shown in Fig. 3.

The invention further provides a method for forming abrupt doping comprising the steps of forming a layered structure of semiconductor material, selectively amorphizing a first layer

20   having a high Ge content greater than 0.5, and crystallizing the amorphized first layer by solid phase regrowth. The amorphized first layer may be formed by ion implantation.

The invention further provides a field effect transistor

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comprising a single crystal substrate having source and drain regions with a channel therebetween and a gate electrode above the channel to control charge in said channel and a first layer of Ge less than the critical thickness doped with a dopant of phosphorus or arsenic positioned below the channel and extending through the source and drain regions.

The invention further provides a field effect transistor comprising a single crystal substrate, a first layer of Ge less than the critical thickness formed on the substrate and doped with a dopant of phosphorus or arsenic, a second layer of undoped SiGe epitaxially formed on the first layer, a third layer of strained undoped simiconductor material of Si or SiGe, a source region and a drain region with a channel therebetween and a gate electrode above the channel to control charge in the channel.

The invention further provides a field effect transistor comprising a single crystal substrate, an oxide layer formed on the substrate having an opening, a gate dielectric and a gate electrode formed in the opening over the substrate, a source and drain region formed in the substrate aligned with respect to the gate electrode, a dielectric sidewall spacer formed on either side of the gate electrode and above a portion of the source and drain regions, a first layer of Ge less than the critical thickness doped with a dopant of phosphorus or arsenic selectivel position over exposed portions of the source and drain regions, a second layer of

semiconductor material selected from the group consisting of Si and SiGe doped with a dopant of phosphorus or arsenic epitaxially formed over the first layer to form raised source and drain regions.

5   Brief Description of the Drawing

These and other features, objects, and advantages of the present invention will become apparent upon consideration of the following detailed description of the invention when read in conjunction with the drawing in which:

10   Fig. 1 is a graph of P concentration versus depth in a SiGe substrate showing an actual concentration profile of the prior art.

Fig. 2 is a graph of P concentration versus depth in a SiGe substrate showing an actual concentration profile to a desired profile.

15   Fig. 3 is a cross section view of a first embodiment of the invention.

Fig. 4 is a graph of P dopant concentration versus depth and of Ge in $Si_{1-x}Ge_x$ versus depth illustrating the invention.

Fig. 5 is a graph of P concentration versus PH_3/He mixture

flow rate in SCCM.

Fig. 6 is a graph of measured conductance versus depth as layers are removed and the projected P concentration versus depth in the layer.

5   Fig. 7 is a cross section view of a layered structure.

Fig. 8 is a cross section view of a layered structure having an amorphized layer.

Fig. 9 is a cross section view of a second embodiment of the invention.

10   Fig. 10 is a cross section view showing an intermediate step in forming the embodiment of Fig. 11.

Fig. 11 is a cross section view showing a third embodiment of the invention.

Fig. 12 is a cross section view showing a fourth embodiment of
15   the invention.

Description of the Preferred Embodiments

Referring to the drawing and in particular to Fig. 3, a cross

section view of structure 30 having an abrupt phosphorus or arsenic profile or abrupt layer doping (ALD) is shown. A substrate 32 having an upper surface 33 may be for example single crystal Si or SiGe. A first layer 36 of 100 % or substantially Ge is epitaxially formed on upper surface 33 having a thickness less than the critical thickness and may be, for example, .5 to 2 nm and is doped with P or As.

The effect of the thickness of first layer 36 is not to increase the doping concentration of P or As, but the effect is to increase the sheet dose, which is the doping concentration multiplied by the doped layer thickness. The doping concentration is controlled by the flow rate of the dopant source gas and by the growth rate of first layer 36, which in turn, is controlled by the flow rate of the Ge source gas which may be, for example, GeH_4.

The critical thickness of a layer is the thickness after which the layer relaxes to relieve strain due to lattice mismatch which for a Ge layer is about 1.04 the lattice spacing of a Si layer. Normally, the mechanism for relieving strain is the generation of crystal lattice defects e.g. misfit dislocations which may propagate to the surface in the form of threading dislocations. A relaxed layer is no longer lattice matched to the layer below.

First layer 36 is substantially Ge and may be 100% Ge. A

second layer 40 comprising Si or SiGe doped to any desired level is formed over first layer 36. Second layer 40 may be formed in a UHV-CVD reactor with a dopant source gas such as PH_3. A Si source gas such as SiH_4 or Si_2H_6 and a Ge source gas such as GeH_4 may be used. A third layer 44 comprising doped or undoped Si or SiGe may be formed in a UHV-CVD reactor over second layer 40.

A UHV-CVD reactor suitable for use in depositing first layer 36, second layer 40 and third layer 44 is available from Leybold-Heraeus Co., Germany and is described in US Patent 5,181,964 which issued Jan. 26, 1993 to B.S. Meyerson and in US Patent 5,607,511 which issued Mar. 4, 1997 to B.S. Meyerson which are incorporated herein by reference. The operation of the reactor and suitable methods for depositing Si and SiGe films is described in US patent 5,298,452 which issued Mar. 29, 1994 to B.S. Meyerson and which is incorporated herein by reference.

Referring to Fig. 4, secondary ion mass spectroscopy (SIMS) data was obtained from a multilayered structure of $Si_{1-x}Ge_x$ doped with phosphorus. In Fig. 4, the ordinate on the right side represents Ge relative intensity with respect to curve 50 and the abscissa represents approximate depth in microns below the surface of the multilayered structure. The structure at a depth of 1.17 μm is 100% Si with the amount of Ge, X equal to zero. As shown by level curve portions 51-57 on curve 50, the amount X of Ge is 0.05

at from 1.12 to 1.08 µm, 0.10 at from 1.03 to 0.99 µm, at 0.15 from

0.93 to 0.59 µm, 0.20 from 0.52 to 0.24 µm, 0.25 from 0.2 to 0.17

µm, 1.0 from 0.17 to 0.13 µm, and 0.25 from 0.13 to 0.3 µm,

respectively.   The layers were epitaxially grown over a single

5   crystal substrate by varying the flow rate of GeH_4. Curve 60 shows

the in-situ phosphorus doping in the multilayers as a function of

depth using PH_3 as the dopant source gas. In Fig. 4, the ordinate

on the left side represents P concentration (atoms/cc) with respect

to curve 60 and the abscissa represents depth.   The 100% seed layer

10   of 0.5-2nm at the depth of 0.17 µm allows for a very abrupt

phoshorus doping profile to occur as shown by curve 60 and

particularly at curve portion 62-63, in Fig. 4 and at the same time

allows for high doping P concentrations to be achieve controllably

as shown by curve 70 in Fig. 5.

15   Fig. 5 is a graph of the phosphorus concentration (atoms/cc)

versus 100 PPM PH_3/He mixture flow (SCCM). In Fig. 5, the ordinate

represents phosphorus concentration (atoms/cc) and the abscissa

represents flow (SCCM).

Due to the limitation of the SIMS technique to resolve very

20   thin layers, the SIMS result shown in Fig. 4 gives a dopant profile

width of about 150-200 Å at full width half maximum (FWHM).   To

better resolve the dopant profile, Hall measurements were used to

measure and profile the active carriers throughout the doped sample

by stepwise etching through the entire doped structure coupled with

direct Hall measurement after each etching step.

Fig. 6 is a graph showing the conductance versus depth and showing
the phosphorus concentration versus depth in a multilayered
structure using direct Hall measurements. In Fig. 6 the ordinate
on the left side represents conductance (mS) and the abscissa
represents depth below the surface of a multilayered $Si_{1-x}Ge_x$
structure having a layer of 1-2 nm Ge at a depth of 115 nm. Curve
80 shows the conductance as measured versus depth. The conductance
increases from 0 at 120 nm to 0.21 at 110 nm. The dopant profile
as measured by the electrical measurement is shown by curve 88.
Curve 80 and/or its data points were used to generate curve 88
shown in Fig. 6 which shows the actual phosphorus doping profile.
Curve 88 was generated by dividing the carrier density as
determined from the conductance shown by curve 80 at the respective
etched depth by the etch layer thickness. In Fig. 6, the ordinate
on the right side represents P concentration (atoms/cc). Curve 86
shows the projected concentration based on curve 88 which shows the
peak concentration rising abruptly from less than 1×10^{15} at 121
nm to 5×10^{19} at 115 nm corresponding to a 13Å per decade rise in
P concentration. The FWHM based on curve 86 which itself is
projected from curve 88 is 8 nm at a peak concentration of 2×10^{19}
atoms/cc. The doping concentration as shown by curve 86 decreases
from 5×10^{19} atoms/cc at 115 nm to about 8×10^{17} atoms/cc at 109
nm and 1×10^{17} atoms/cc at 64.9 nm. The decrease in P
concentration from 115 nm to 64.9 nm corresponds to a 20 nm per

decade fall or decrease in P concentration.

It is noted that PH_3 has a sticking coefficient S of 1.0 while SiH_4 has a sticking coefficient S of 1×10^{-3} to 1×10^{-4}. The doping profile of P is a function of 1/GR where GR is the growth rate of the film.

Further, to eliminate background autodoping when an abrupt reduction in the P concentration is desired, a growth interrupt method is provided. The substrates or wafers are removed from the growth chamber or UHV-CVD to another vacuum chamber such as a load lock or transfer chamber or another UHV-CVD reactor or furnace where no PH_3 has been flown prior to loading. Then, SiH_4 and GeH_4 gases are flown in the growth chamber to coat the walls or heated surfaces of the growth chamber to bury or to isolate the P on the sidewalls. Then, the substrates or wafers are introduced or moved back into the main or growth chamber and the growth of Si or $Si_{1-x}Ge_x$ is continued. Alternatively, another UHV-CVD reactor or furnace coupled to the transfer chamber may be used to continue the growth of Si or SiGe with reduced or no P or As doping.

Another method for achieving abrupt P doping, is to grow a first epitaxial layer 80 in the range from 1 to 10 nm thick of $Si_{1-x}Ge_x$ on a substrate 82 as shown in Fig. 7. The higher the value of X the better for converting layer 80 to amorphous material by ion implantation by ions 83 shown in Fig. 8; X may be, for example,

greater than 0.5. First epitaxial layer 80 may be unstrained or a strained layer due to lattice mismatch with respect to substrate 82. A second epitaxial layer 84 may be grown over first epitaxial layer 80. Layer 84 may be Si or SiGe and may be unstrained or

5   strained. Then using ion implantation shown in Fig. 8, the first epitaxial layer 80 may be selectively amorphized to form layer 80' shown in Fig. 8 by ions 83 with respect to layer 84 and substrate 82 at a dose in the range from about 10^{13} to about 10^{14} atoms/cm^2 or higher; layer 84 and any other Si or SiGe layers will not be

10   amorphized. The Ge content of layer 84 and the other layers should be less than the content X in layer 80.

The critical dose for amorphization depends on the implanted species as well as on the host lattice. For example, boron does

15   not amorphize Si at any dose, but amorphizes Ge at a dose higher than 1×10^{14} atoms/cm^2. Asenic amorphizes Si at a dose of about 5 $\times 10^{14}$ atoms/cm^2, while Arsenic amorphizes Ge at a dose of 1×10^{13} atoms/cm^2. Thus if an implant dose below the amorphization threshold in Si but above that in SiGe or Ge is used, then only the

20   SiGe or Ge will be amorphized. The dossage peak should be adjusted to occur at the depth of the layer to be amorphized, layer 80.

Substrate 82 and first epitaxial layer 80 is then heated to a temperature in the range from 400°C to 500° for a period of time such as from 1 to 5 hours which results in solid phase

recrystallization of the amorphized layer to form $Si_{1-x}Ge_x$ layer 80'' shown in Fig. 9.

Recrystallization of amorphous layer 80' is dependent upon the material of the layer. Amorphous Ge recrystallizes at a temperature T greater than 350°C, while Si recrystallizes at a temperature T greater than 500°C. The combination of amorphization threshold dose and recrystallization temperature difference between Si and Ge is key to provide recrystallized layers.

The alloy SiGe recrystallization temperature will be somewhere in between Si and Ge, depending on the Ge content. If thicker doped layers are sought, which are above the critical thickness of Ge on Si, then SiGe with the highest possible Ge content (that will stay strained) should be used. To maximize the sharpness of the doping profile, the layers surrounding the doped layer should have the lowest possible Ge content (depending on the design).

Dopant activation occurs only in layer 80''. Thus the doped layer thickness 80'' is determined by the original epitaxial layer thickness 80. Diffusion of P dopants at the recrystallization temperature is negligible.

The above method applies to any species and not just to P. In fact getting sharp p-type implants is very much needed in the channel implant of 0.25μm PMOS and will be needed more when the

gate length is shrunk. B cannot be used for such super retrograde profiles, and hence people have resorted to heavy ions such as In. However, the degradation in channel mobility is higher in that case, and the incorporation of In at levels higher than 5×10^{17} atoms/cm^3 is almost impossible.

An n or p channel field effect transistor 91 is shown in fig. 9 utilizing layer 80''. A dielectric layer 85 may be formed on the upper surface of layer 84 to form a gate dielectric such as silicon dioxide. A gate 86 may be blanket deposited and patterned above dielectric 85 which may be polysilicon. Self aligned shallow souce and drain regions 87 and 88 may be formed in layer 84 by ion implantation using gate 86 as a mask. Sidewall spacers 89 and 90 may be formed on the sidewalls of gate 86. Source and drain regions 87' and 88' may be formed in layers 80 and 84 and substrate 82 using sidewall spacers 89 and 90 as a mask. Source 87 and 87' and drain 88 and 88' may be of one type material (n or p) and layer 80'' may be of the opposite type material. Layer 80'' functions to adjust the threshold voltage of the field effect transistor 91, prevent short channnel effects and prevent punch through between source and drain.

Referring to Fig. 10, an intermediate step in forming a field effect transistor is shown. A substrate 95 may be relaxed undoped SiGe. A phosphorous-doped Ge layer 96 is formed thereover as described with reference to Figs. 3 of 9. An undoped SiGe layer 97

is formed over layer 96. A strained undoped Si layer 98 may be formed over layer 97. Layer 98 is suitable for an electron or hole gas 99 to be present under proper voltage biasing conditions.

Referring to Fig. 11, field effect transistor 102 is shown. In fig. 11, like reference numbers are used for functions corresponding to the apparatus Fig. 10. Source and drain regions 103 and 104 are formed spaced apart through layers 96-98 and into substrate 95. A gate dielectric 105 may be formed over layer 98 in the region between source 103 and drain 104. A gate electrode 106 of polysilicon or metal may be blanket deposited and patterned. Alternately, gate dielectric 105 may be deleted and a gate electrode of metal may form a Schottky barrier with layer 98.

Referring to Fig. 12, a cross section view of field effect transistor 110 is shown with raised source 40' and drain 40''. In Fig. 12 like references are used for functions corresponding to the apparatus of Figs. 3 and 9. Substrate 82' has a layer of field oxide 112 thereover with an opening 113 formed therein. In opening 113, a gate dielectric 85 is formed on substrate 82'. A gate electrode 86 is formed such as from polysilicon and a shallow source 87 and drain 88 are formed by, for example, ion implantation self aligned with respect to gate electrode 86. Next, sidewalls 89 and 90 are formed on either side of gate electrode 86. Next, a layer 36' is selectively formed epitaxially on shallow source 87 and drain 88 on substrate 82'which is phosphorous or arsenic doped.

Layer 36' is Ge or substantially Ge and corresponds to layer 36 in Fig. 3. Above layer 36', layer 40' of Si or SiGe is selectively formed epitaxially which is phosphorous or arsenic doped during fabrication. Layer 40' forms source 117 above shallow source 87 and forms drain 118 above shallow drain 88. Metal silicide contacts (not shown) may be made to source 117 and drain 118.

While there has been described and illustrated a structure having an abrupt doping profile and methods for forming an abrupt profile, it will be apparent to those skilled in the art that modifications and variations are possible without deviating from the broad scope of the invention which shall be limited solely by the scope of the claims appended hereto.